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THERMOELECTRIC VAPOR PRESSURE OSMOMETRY

by

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ABSTRACT. The thermoelectric vapor pressure osmometer is established as a satisfactory instrument for the determination of the vapor pressure lowering of solutes in solutions. The calibration constant, a_1 , of the instrument is demonstrated to be independent of the nature of the solute and can be calculated from a knowledge of the system geometry and measurable thermodynamic and transport parameters.

Experimental results are evaluated in terms of the change in resistance of the thermistor and the concentration of solution. It is necessary to use a second-degree equation in concentration plot to fit the data. Evaluation of the coefficient of the second-order term requires the incorporation of a heat-of-mixing term in the form of the Van Laar equation. The concentration-independent term β for the heat of mixing is obtained for fourteen solute-solvent pairs.



U. S. NAVAL ORDNANCE TEST STATION
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March 1967

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FOREWORD

This work was undertaken to provide a theoretical basis for a solute characterization method used in evaluation of prepolymers useful in propellants. The report describes studies performed under Bureau of Naval Weapons Task Assignment RMMP-22-066/216-1/R001-06-01, P.A. #2, FY 1965 and 1966, and Naval Ordnance Systems Command Task Assignment 033-129/200-1/R001-06-01, P.A. #2, FY 1967.

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Released by
WILLIAM S. McEWAN, Head
Chemistry Division
8 December 1966

Under authority of
HUGH W. HUNTER, Head
Research Department

NOTS Technical Publication 4247

Published by.....Research Department
Collation.....Cover, 14 leaves, DD Form 1473, abstract cards
First printing.....190 unnumbered copies
Security classification.....UNCLASSIFIED

INTRODUCTION

Interest in a rapid and precise method for measuring the number-average molecular weight of low molecular weight polymers and prepolymers has increased within the last few years. The thermoelectric technique has become popular in the range of molecular weights of polymers below 10,000. Ebullioscopic and cryoscopic methods require difficult differential techniques for the highest sensitivity and are often tedious and time-consuming. These methods are complicated by a limited choice of solvents, foaming, coprecipitation, solvation, and molecular stability. The thermoelectric method on the other hand is rapid, requires small samples, and permits a wide choice of solvents. In addition, this method was recently reported to have been extended to polymers of 40,000 molecular weight (Ref. 1).

It, therefore, became of interest to determine the extent to which a popular, commercially available instrument for thermoelectric determinations could be used as a research tool, and, if possible, determine the necessary conditions for its proper use as such a tool.

A number of authors (Ref. 1-14) have utilized the method of Hill (Ref. 15) to measure either vapor pressure differences or, from these differences, molecular weights of solutes.

A paper by Tomlinson and co-workers (Ref. 12) has reviewed vapor pressure osmometry and calculated thermodynamic efficiencies for a number of solvent systems, and Van Dam (Ref. 13) has optimized a thermoelectric vapor pressure osmotic system using thermocouples and a detailed analysis of the mass and heat transport to measure molecular weights up to 14,000. Van Dam has estimated the upper limit of this method to be 30,000 with an accuracy of 10%.

Calculations of molecular weight using the vapor pressure osmometer are based upon a calibration of the instrument with a purified, low molecular weight solute of known molecular weight. This constant is often called the calibration constant and has been calculated from dimensions of the instrument, thermal balance factors such as solvent evaporation from the cell, thermal conduction, solute diffusion through the drop, and diffusion of solvent through the cell atmosphere by Tomlinson (Ref. 12). The calibration constant is called d by Tomlinson and K by Burge (Ref. 5). In this report, the calibration constant is designated by a_1 . A derivation is presented below.

Equation 1 is the conventional Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{\Delta H_v}{RT^2} \quad (1)$$

where p is the vapor pressure of solvent, T is the absolute temperature in degrees Kelvin, R is the gas constant in kilocalories per mole per degree, and ΔH_v is the heat of vaporization of the solvent in kilocalories per mole. For small changes in temperature and vapor pressure, Eq. 1 can be rewritten in transposed, approximate form as Eq. 2.

$$\Delta T = \frac{RT_o^2}{\Delta H_v} \ln \frac{p}{p_o} \quad (2)$$

where $\Delta T = T - T_o$, T_o is some reference temperature, and p_o is the vapor pressure of pure solvent at T_o .

The variation in the resistance, r , in ohms, of a thermistor with temperature can be written as Eq. 3 (Ref. 4 and 8).

$$\frac{d \ln r}{dT} = -\frac{B}{T^2} \quad (3)$$

This equation was carefully verified by Müller and Stolten (Ref. 8) and by the authors of this report (Fig. 1). The constant B is the semiconductor constant with the dimensions of degrees Kelvin. For small changes in resistance and temperature, Eq. 3 can be approximated, rewritten, and transposed as Eq. 4

$$\Delta T = -\frac{T_o^2}{B_2} \ln \frac{r_2}{r_{2,o}} \quad (4)$$

where $r_{2,o}$ is the resistance of the solution thermistor at T_o .

Since Eq. 2 and 4 refer to the same temperature change, these equations yield Eq. 5

$$\ln \frac{r_2}{r_{2,o}} = -\frac{B_2 R}{\Delta H_v} \ln \frac{p}{p_o} \quad (5)$$

To use Eq. 5 in a two-thermistor system with one bead for pure solvent and a second bead for solution it should be understood that the equation is only valid when the semiconductor constants and resistances of the thermistors are carefully matched. Since the system is kept at a constant temperature, this requirement can be eased if the semiconductor constant, B_2 , of the solution thermistor having a resistance,

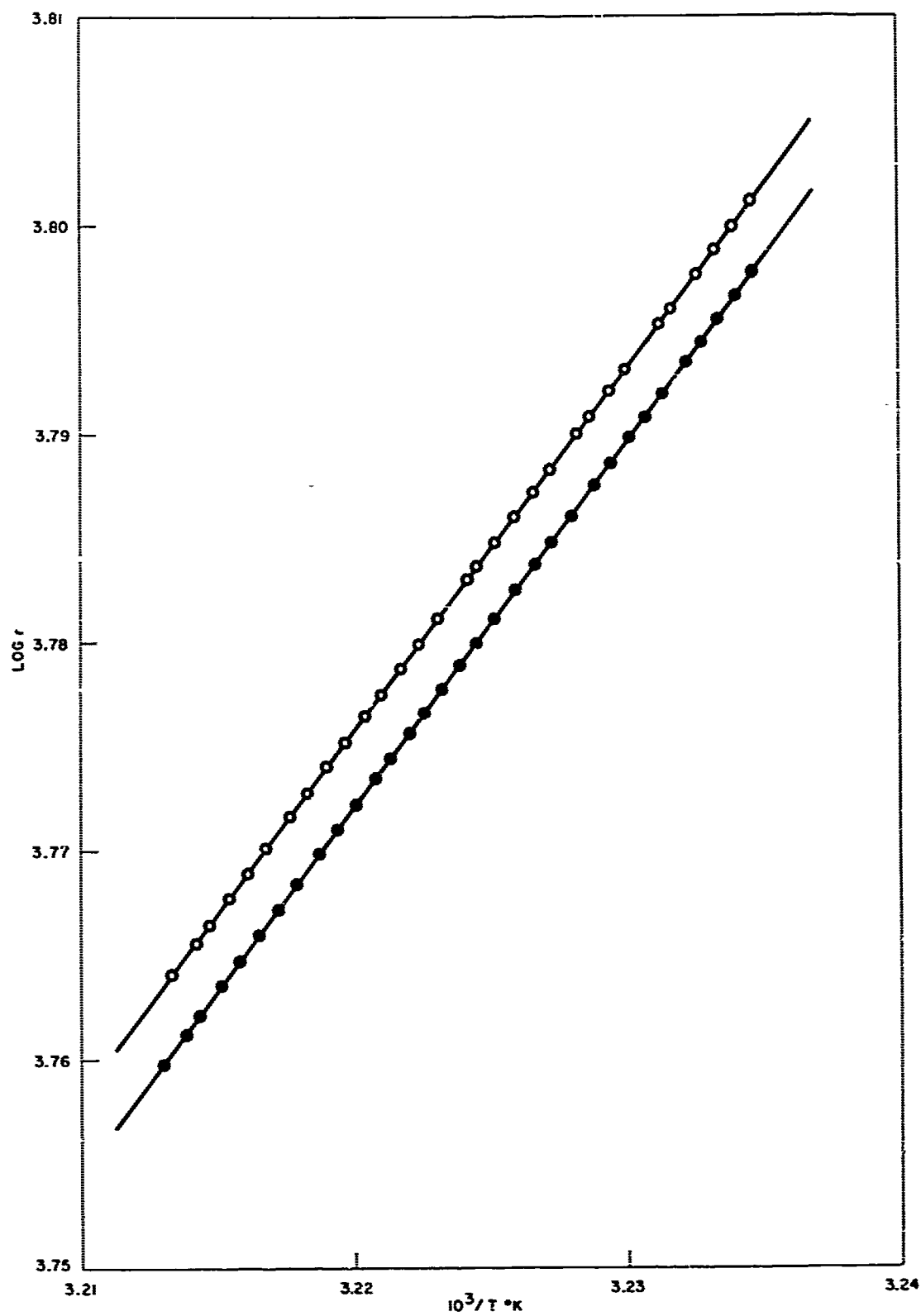


FIG. 1. Plots of $\text{Log } r$ vs. $1/T$ for Reference (o) and Sample (●) Thermistors.

r_2 , is such that, over the temperature-cycling period of the instrument, $r_1 - (r_2 + r_{CB}) < |0.02 \text{ ohm}|$, where r_{CB} is a variable balancing resistor used to compensate for $r_1 \neq r_2$ at T_0 . The variable resistor r_{CB} is selected to be temperature insensitive. A variation in B between the two thermistors of 319°K is permissible as long as the temperature variation during cycling at any one point is less than 10^{-3}°K for the period of measurement.

Application of Raoult's law, Eq. 6, for the variation of vapor pressure with composition

$$\frac{p}{p_0} = (1 - X_2) \quad (6)$$

where X_2 is the mole fraction of solute, is made in Eq. 5

$$\Delta r_2 = - \frac{B_2 R r_{2,0}}{\Delta H_v} \ln (1 - X_2) \quad (7)$$

in which it is assumed that $\ln r_2/r_{2,0} \approx \Delta r_2/r_{2,0}$. For dilute solutions, Eq. 7 reduces to Eq. 8

$$\Delta r_2 \approx \frac{B_2 R r_{2,0}}{\Delta H_v} \cdot X_2 \approx \frac{B_2 R r_{2,0}}{\Delta H_v} \cdot \frac{n_2}{n_1} = \frac{B_2 R M_1 r_{2,0}}{\Delta H_v 10^3} \cdot m_2 \quad (8)$$

where n_1 is the number of moles of solvent, n_2 is the number of moles of solute, M_1 is the molecular weight of the solvent, and m_2 is the molality of the solute.

If the solution density, ρ_g , is assumed to be very nearly equal to the solvent density, ρ_1 , then Eq. 9 is obtained where C is the molarity of the solution.

$$\Delta r_2 = \frac{B_2 R M_1 r_{2,0}}{\Delta H_v \rho_1 10^3} \cdot C \quad (9)$$

that is, $\Delta r_2 = a_1 C$ where $a_1 = \frac{B_2 R M_1 r_{2,0}}{\Delta H_v \rho_1 10^3}$

It was of interest, therefore, to establish the degree to which a_1 is a constant for a number of solutes of differing molecular weights. It was also of interest to explore to some degree the significance and mode of plotting data customarily obtained during a molecular weight determination. To achieve this end, a number of pure model compounds are used covering a range of molecular weights from 135 to 1,238. To

obtain compounds in the higher molecular weight range, use was made of the reaction of a diisocyanate with good samples of the available fluorinated alcohols.

EXPERIMENTAL

SOLUTES

Acetanilide (National Bureau of Standards Microanalytical Standard 141) was used as received. 1,3-Dinitrobenzene (Eastman Kodak Co.) was recrystallized five times from ethanol-water (2:1); m.p. 91.3-91.5°C. Benzil (Fisher Scientific Co.) was recrystallized twice from absolute ethanol; m.p. 95.3-96.0°C. 2,4,6-Tribromoaniline (Eastman Kodak Co.) was recrystallized three times from 95% ethanol; m.p. 121.0°C. Toluene-2,4-dicarbamates were prepared by direct reaction of toluene-2,4-diisocyanate (TDI) and the appropriate alcohol. The synthesis of bis(1,1,7-trihydroperfluoroheptyl) toluene-2,4-dicarbamate illustrates the general procedure. Pure 1,1,7-trihydroperfluoro-1-heptanol (36.5 grams, 0.11 mole), freshly distilled TDI (8.7 grams, 0.05 mole), and a few crystals of ferric acetylacetonate were mixed in a 125-ml Erlenmeyer flask protected with a drying tube. After the exothermic reaction had subsided, the mixture was heated on a steam bath for 1 hour. After cooling, the resultant crystalline mass was crushed under 50 ml of carbon tetrachloride, collected, and washed with two 50-ml portions of carbon tetrachloride. The product was then repeatedly recrystallized from the appropriate solvent to a constant melting point. The data for the dicarbamates are presented in Table 1.

SOLVENTS

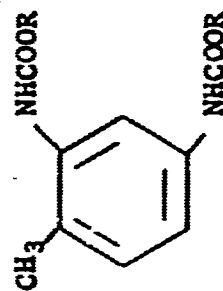
Toluene (reagent grade), acetone (electronic grade), and 1,2-dichloroethane (technical grade) were all obtained from Baker and Adamson Products and were used without further purification.

1,2-Dimethoxyethane (Eastman Kodak Co.) was dried over CaH_2 and LiAlH_4 and then distilled from fresh LiAlH_4 through an Oldershaw column. A middle fraction was collected; b.p. 81.7°C/710 mm.

INSTRUMENTATION

All measurements are made with a vapor pressure osmometer (Model 301A) manufactured by Mechrolab, Inc., Mountain View, California. In this instrument the temperature of the solvent-vapor chamber is held constant to $\pm 0.001^\circ\text{C}$ or better by means of a mercury thermostat preset

TABLE 1. Properties of Toluene-2,4-dicarbamates



R	Recrystallization solvent	M.p., ^a °C	Formula	Analysis, %							
				Calculated				Found			
				C	H	F	N	C	H	F	N
$\text{CH}_3(\text{CH}_2)_5$	Acetonitrile-water (3.35:1)	84.3-85.1 ^b	$\text{C}_{21}\text{H}_{34}\text{N}_2\text{O}_4$	66.63	9.05	7.40	66.82	9.07	7.45
$\text{CF}_3(\text{CF}_2)_2\text{CH}_2$	Acetonitrile-water (4.65:1)	119.9-120.7 ^c	$\text{C}_{17}\text{H}_{12}\text{F}_{14}\text{N}_2\text{O}_4$	35.55	2.11	46.32	4.88	35.84	2.15	46.15	4.80
$\text{H}(\text{CF}_2)_6\text{CH}_2$	1,2-Dichloroethane	102.7-103.4	$\text{C}_{23}\text{H}_{14}\text{F}_{24}\text{N}_2\text{O}_4$	32.95	1.68	54.39	3.34	32.80	1.66	54.07	3.52
$\text{H}(\text{CF}_2)_{10}\text{CH}_2$	Benzene-ethyl acetate (1:1)	153.5-154.0	$\text{C}_{31}\text{H}_{14}\text{F}_{40}\text{N}_2\text{O}_4$	30.06	1.14	61.37	2.26	29.96	1.28	61.20	2.27

^a All melting points were determined using a Kofler hot stage.^b Literature m.p. 83°C (Ref. 16).^c Previously prepared by R. A. Henry of this Station, m.p. 117-118°C, F, 46.32%.

to $37 \pm 0.2^\circ\text{C}$. The sensing elements are two, well-matched, bead thermistors. The variation of the resistance of the thermistors with temperature is measured over a range of about 2°C in the vicinity of 37°C . These data are plotted in form of $\log_{10} r$ vs. $1/T$ as seen in Fig. 1. The matching of these thermistors is listed in Table 2. The Leeds and Northrup d.c. null detector amplifier, which is driven by a d.c. Wheatstone bridge, proves to be extremely stable over long periods of operation and requires only infrequent and small adjustments to null zero.

TABLE 2. Resistance-Temperature Characteristics of VPO Thermistors at 37°C

Thermistor	Resistance, ohms	Temperature coefficient, ohm/ohm/ $^\circ\text{C}$	Semiconductor constant B, $^\circ\text{K}$
Reference	6,064	-0.0416	4,004
Sample	6,016	-0.0419	4,030

When measurements were attempted with a volatile solvent such as acetone, solvent was lost from the sample syringe because of capillary attraction between the ground surfaces of the plunger and barrel. This loss of the solvent resulted in a slow increase in the observed Δr value when replicate measurements were made on a sample solution. To overcome this difficulty the instrument was equipped with gas-tight syringes each having a Teflon-tipped plunger fabricated by the Hamilton Co., Whittier, California. These syringes have the same general dimensions as those supplied with the instrument and, therefore, no modification of the syringe holder was required. Using the new syringes, sample solutions can be left in the thermal block for several hours without a detectable drift in the Δr values. The improved syringe is shown in Fig. 2.

MEASUREMENT TECHNIQUE

Solutions used in measurements of Δr are prepared immediately before use by direct weighing of the solute into a 25-ml volumetric flask. Measurements are carried out under as nearly identical conditions as possible. Syringes are placed in the thermal block and allowed to come to chamber temperature over a period of at least 15 minutes. The technique employed in zeroing and balancing the instrument is essentially the same as that suggested by the manufacturer. Subsequently, a drop of the test solution is placed on the sample thermistor and readings of Δr are taken at intervals up to 6 or 8 minutes to establish an optimum reading time. At least four readings are taken at each concentration of the test solution.

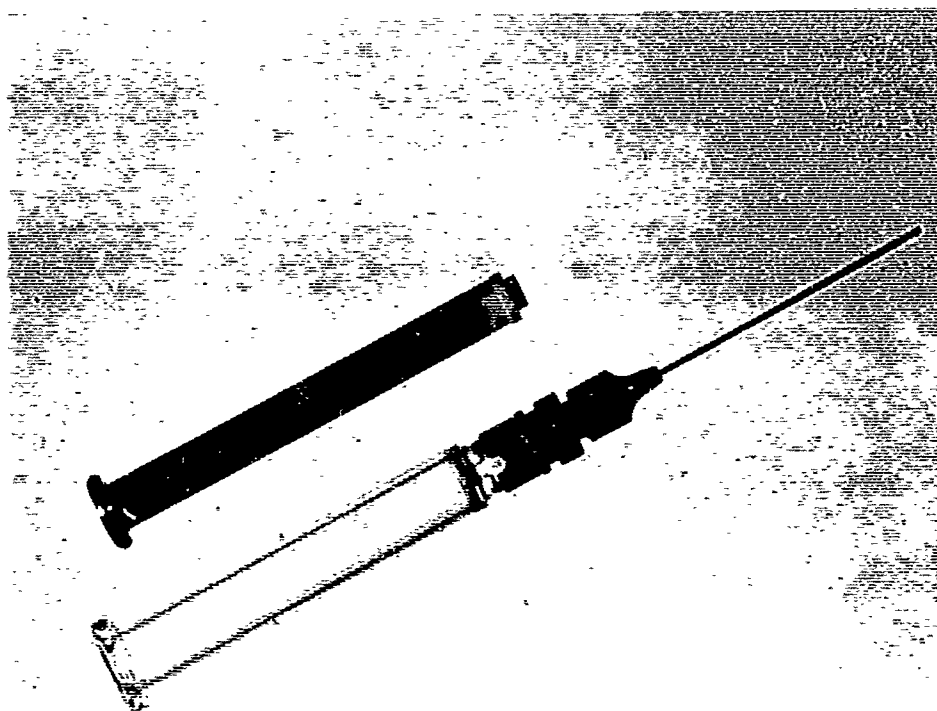


FIG. 2. Gas-tight Syringe With Teflon-tipped Plunger.

Calibration runs are made at concentrations up to about 0.04 mole/liter in acetone and in 1,2-dichloroethane and to about 0.07 mole/liter in toluene and in 1,2-dimethoxyethane.

CALCULATIONS

The calculations were done on an IBM 7094 digital computer using a program written in FORTRAN IV language. The program was arranged to yield the least-squares best estimates of the first, a_1 , and second, a_2 , virial coefficients of the quadratic expression

$$\Delta r = a_1 C + a_2 C^2 \quad (10a)$$

as well as the calculated values of the dependent variable, $\Delta r'$, the vertical deviations of the observed points from the sample regression line, $\Delta r - \Delta r'$, and the standard error of estimate, $s_{y|x}$.

When $a_2 = 0$, Eq. 10a reduces to Eq. 9.

RESULTS AND DISCUSSION

A careful examination of the representative calibration data for the four solvent systems, that is, toluene (Fig. 3), 1,2-dichloroethane (Fig. 4), 1,2-dimethoxyethane (Fig. 5), and acetone (Fig. 6), plotted in the form of Eq. 9, reveals a curvature indicating the necessity of a consideration of the data in the form of a higher order concentration equation as Eq. 10a. Table 3 presents the data obtained for a number of solutes in four solvent systems with the various measured constants defined by Eq. 10a. This form was used rather than that of Eq. 10b

$$\frac{\Delta r}{C} = a_1 + a_2 C \quad (10b)$$

(Ref. 17) since plotting the data in the form of Eq. 10b has, in several cases, tended to give the plotted line an upward curvature for data obtained at low concentrations. In addition, an attempt was made to establish whether the use of an additional constant, a_0 , as in Eq. 11

$$\Delta r = a_0 + a_1 C + a_2 C^2 \quad (11)$$

could improve the fit of the data by allowing this constant to assume nonzero values (Ref. 18). Some consideration was also given in preparing the computer program to introduce a third concentration dependent term as in Eq. 12.

$$\Delta r = a_0 + a_1 C + a_2 C^2 + a_3 C^3 \quad (12)$$

The analysis of these data indicated that no significant improvement was obtained in the standard error of estimate by assuming $a_0, a_3 \neq 0$. In fact, a better fit of the data is obtained by requiring that $a_0 = 0$.

EVALUATION OF CONSTANTS a_1 AND a_2

A good thermodynamic treatment of solutions (Ref. 19) can be used to evaluate the virial coefficients, a_1 and a_2 . First, it should be noted that Eq. 6 is a special case of Eq. 13

$$\frac{P}{P_0} = (1 - X_2) \exp(\Delta h_0/RT) \quad (13)$$

where Δh_0 , the heat of dilution, is zero for ideal solutions. Incorporating this term and defining Δh_0 by Eq. 14

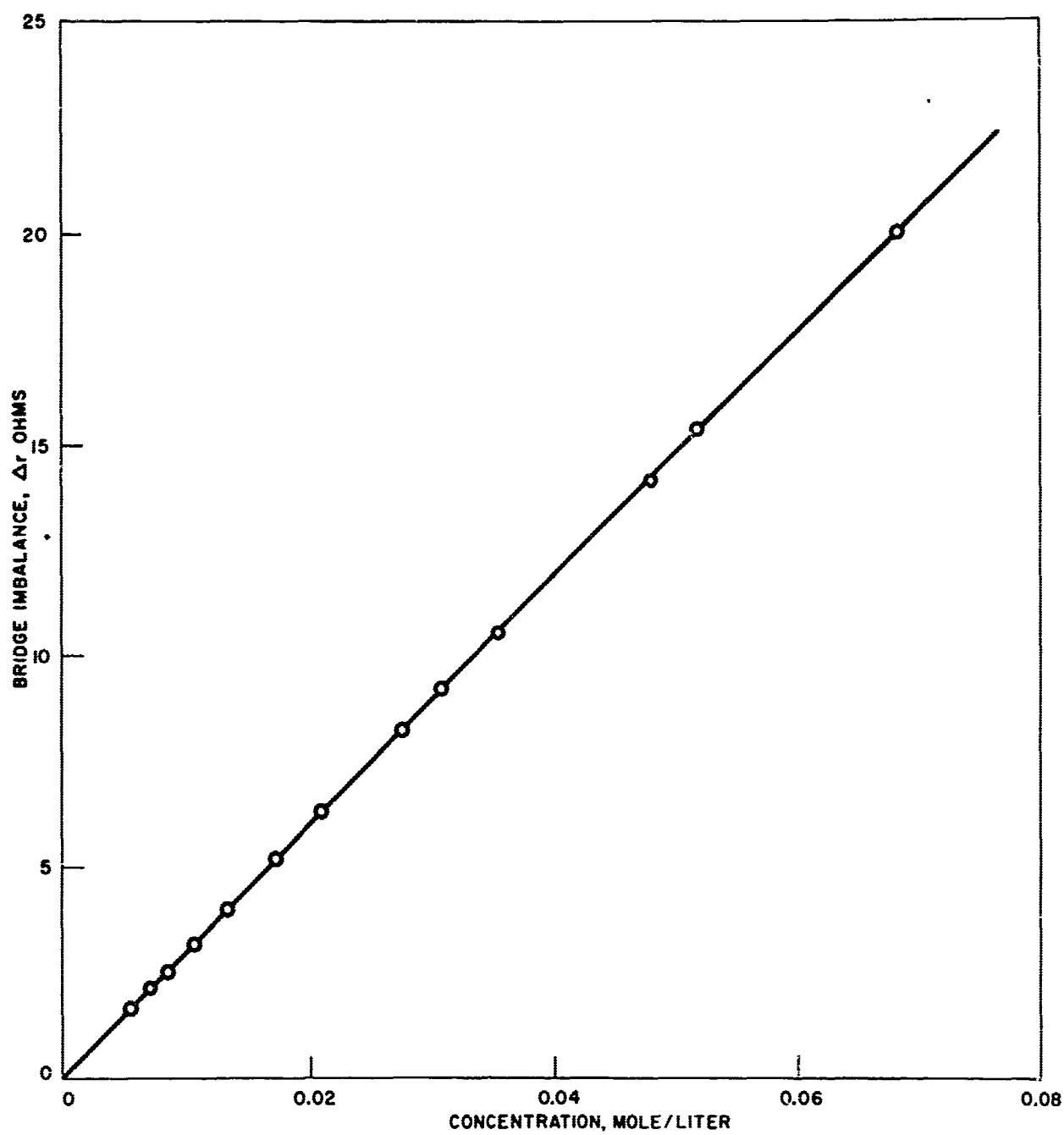


FIG. 3. Calibration Curve for 2,4,6-Tribromoaniline in Toluene at 37°C.
Reading time: 3 minutes.

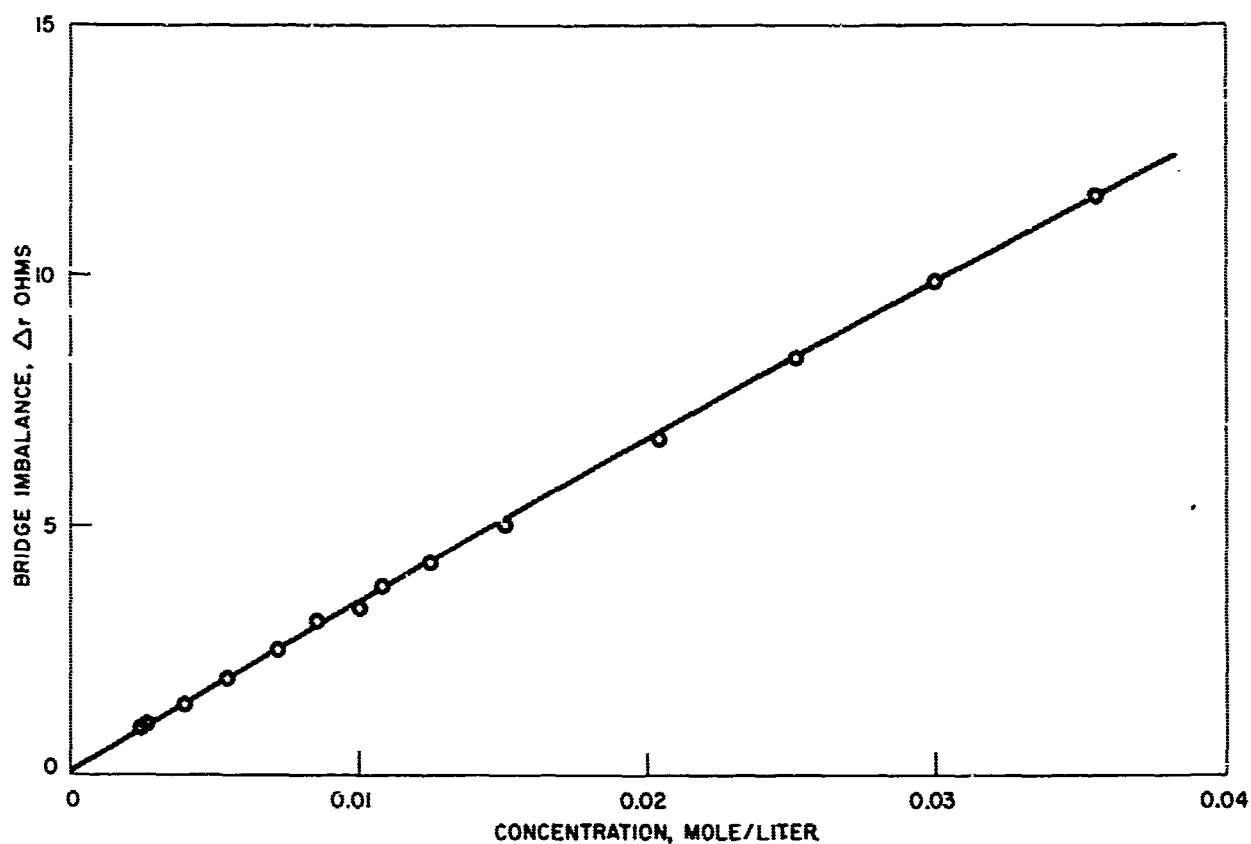


FIG. 4. Calibration Curve for Benzil in 1,2-Dichloroethane at 37°C.
Reading time: 3 minutes.

$$\Delta h_o = \beta \bar{v}_2^2 \quad (14)$$

where β is the Van Laar heat of mixing and \bar{v}_2 is the volume fraction of solute, Eq. 15a and 15b can be derived in a manner similar to the derivation of Eq. 9.

$$\Delta r_2 = \frac{B_2 R r_{2,o}}{\Delta H_v} \left[\frac{M_1}{\rho_1 10^3} C + \left(\frac{M_1^2}{2 \rho_1^2 10^6} - \frac{\beta M_2^2}{RT_o \rho_2^2 10^6} \right) C^2 \right] \quad (15a)$$

$$\Delta r_2 = \frac{B_2 R r_{2,o}}{\Delta H_v} \left[\frac{M_1}{\rho_1 M_2 10^3} C_w + \left(\frac{M_1^2}{2 M_2^2 \rho_1^2 10^6} - \frac{\beta}{RT_o \rho_2^2 10^6} \right) C_w^2 \right] \quad (15b)$$

where C_w is the weight concentration of solute in grams per liter.

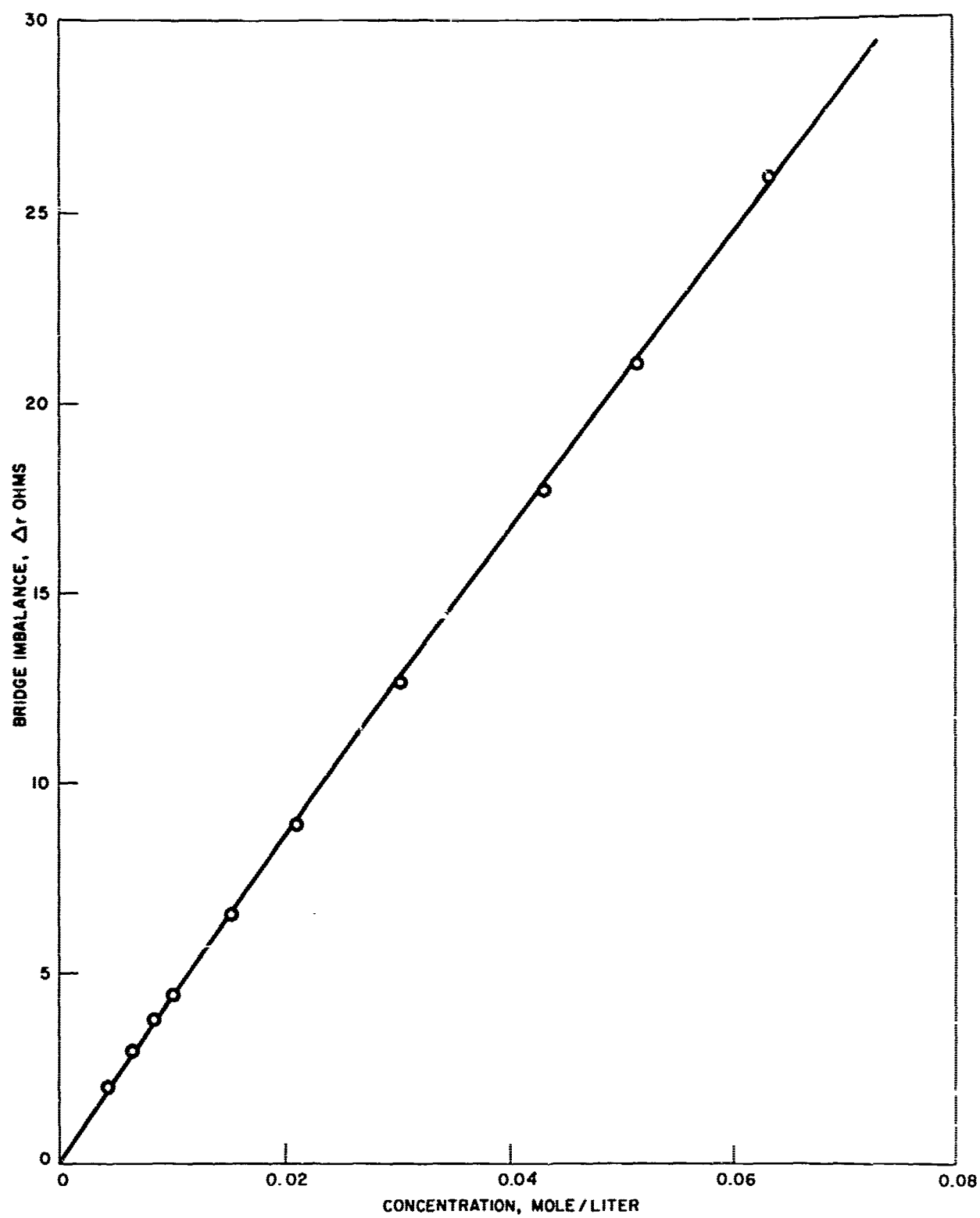


FIG. 5. Calibration Curve for Benzil in 1,2-Dimethoxyethane at 37°C.
Reading time: 6 minutes.

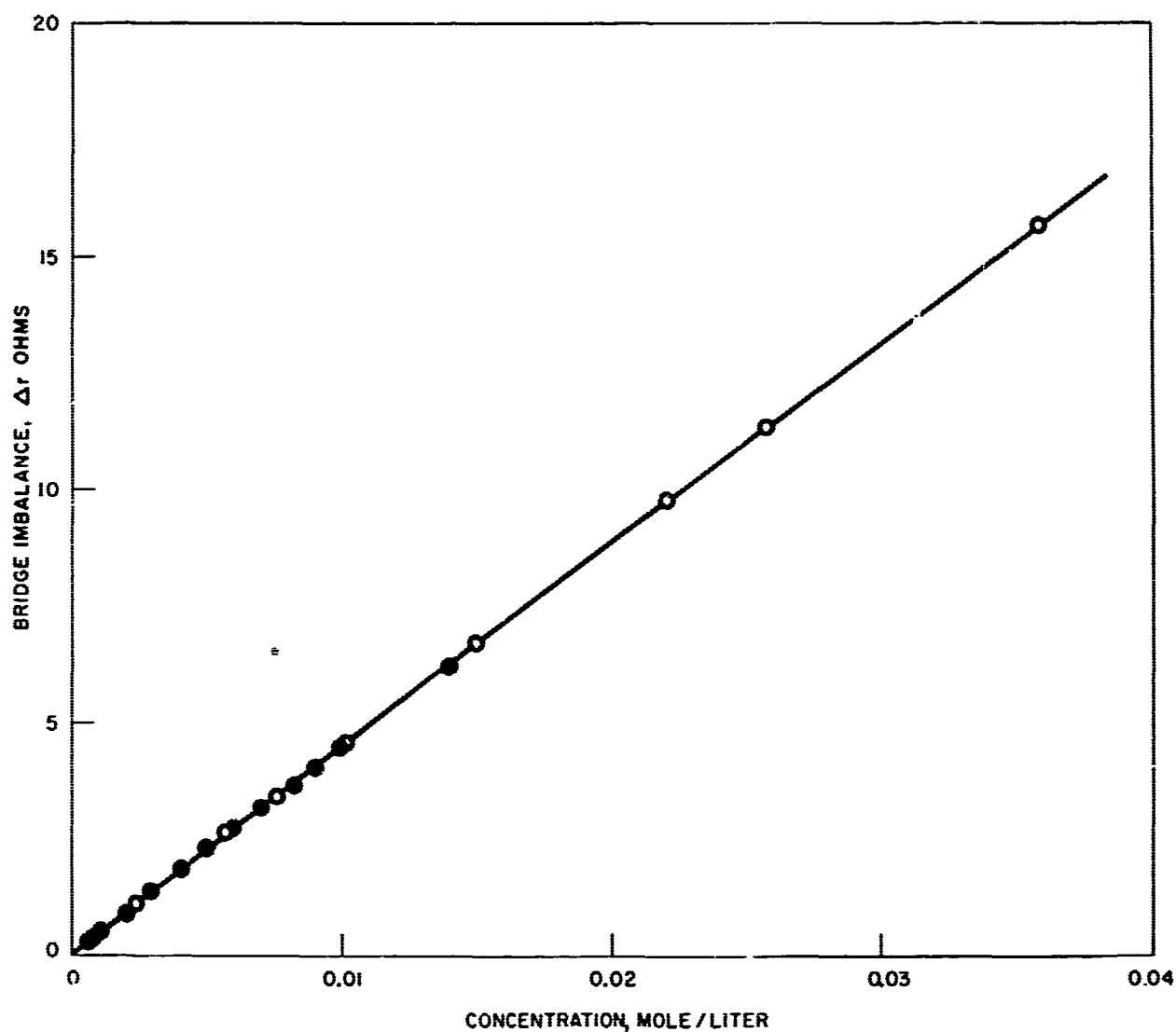


FIG. 6. Calibration Curve for Bis(1,1,11-trihydroperfluoroundecyl) toluene-2,4-dicarbamate in Acetone at 37°C. Reading time: 3 minutes. The filled circles represent data obtained 2 months later.

TABLE 3. Values of the Coefficients in the Equation $\Delta r = a_1C + a_2C^2$ at 37°C

Reading time: 3 minutes.

Solute	Formula weight	a_1 , ohm-liter/mole	a_2 , ohm-liter ² /mole ²	s_y/x , ^a ohm
A. Acetone				
Acetanilide.....	135.16	450	-352	0.04
1,3-Dinitrobenzene.....	168.11	449	-357	0.03
Benzil.....	210.22	455	-377	0.04
2,4,6-Tribromoaniline.....	329.85	453	-416	0.01
Di-n-hexyl toluene-2,4-dicarbamate.	378.50	456	-457	0.04
Bis(1,1-dihydroperfluorobutyl) toluene-2,4-dicarbamate.....	574.28	458	-368	0.03
Bis(1,1,7-trihydroperfluoroheptyl) toluene-2,4-dicarbamate.....	838.36	452	75.9	0.02
Bis(1,1,1,1-trihydroperfluoro-undecyl) toluene-2,4-dicarbamate.	1,238.44	<u>455</u> Ave. 454	-482	0.02
B. 1,2-Dichloroethane				
Benzil.....	210.22	349	-657	0.08
C. 1,2-Dimethoxyethane				
Benzil.....	210.22	431 ^b	-392	0.12
D. Toluene				
Acetanilide.....	135.16	299	-914	0.02
Benzil.....	210.22	302	-118	0.01
2,4,6-Tribromoaniline.....	329.85	302	-155	0.04
Bis(1,1,7-trihydroperfluoroheptyl) toluene-2,4-dicarbamate.....	838.36	<u>299</u> Ave. 301	-911	0.03

^a Standard error of estimate.^b Reading time: 6 minutes.

From Eq. 15a, the coefficients a_1 and a_2 can be defined as

$$a_1 = \frac{B_2 R r_{2,o} M_1}{\Delta H_{v,1} 10^3}$$

$$a_2 = \frac{B_2 R r_{2,o}}{\Delta H_v} \left(\frac{M_1^2}{2 \rho_1^2 10^6} - \frac{\beta M_2^2}{R T_o \rho_2^2 10^6} \right)$$

From Eq. 9 and 15a the constant a_1 can be obtained in terms of measurable system constants. The thermistor constant B is determined from the data presented in Fig. 1. The straight line also establishes the validity of the thermistor resistance-temperature equation over the temperature range of interest. From the evaluation of a_2 , values of β can be calculated.

DETERMINATION OF THE EFFECTIVE HEAT OF VAPORIZATION

The value for the heat of vaporization to be used in Eq. 15a or 15b must be considered. The theoretical heat of vaporization gives values for a_1 that are small; the effective heat of vaporization $\Delta H_{v,eff}$, must therefore, be less than the theoretical heat of vaporization. This problem has been considered in great detail in an excellent publication by Tomlinson and co-workers (Ref. 12).

Tomlinson considers a steady-state thermal balance in which the rate of heat gained by the thermistor through evaporation of the solvent from the cell and diffusion through the cell to the bead thermistor is equal to the rate of heat loss caused by conduction through the gas phase, radiation from the drop, conduction through the thermistor leads, and loss through the thermistor stem.

In this report, the treatment of Tomlinson is applied to calculate the thermodynamic efficiency, η_{calc} , from the various measured system constants. If the thermodynamic efficiency can be calculated, then the constant a_1 can be calculated. The difference in geometry and construction of the Tomlinson apparatus and that used in these experiments is sufficient to begin to evaluate the general nature of the treatment. It should be noted here that the Tomlinson thermistor was encased in a thin glass tube requiring a correction for the thermistor stem. Since no glass stem is used in the construction of the thermistors used here, this correction is not needed. In addition, the thermistor leads are stainless steel rather than platinum and therefore the appropriate stainless steel conductivity is used. Further, the drop size is variable

but is found to vary from about twice the diameter of the thermistor to about three times the thermistor diameter. At three times the thermistor diameter the drop appears almost ready to fall from the bead. Since it has already been demonstrated by a number of workers and verified by the authors of this report that the results are quite independent of the drop size, a value for the drop diameter of twice the thermistor diameter is assumed. In the thermodynamic efficiency calculations with the drop diameter assumed to be three times the thermistor diameter, the change in calculated thermodynamic efficiency is very slight.

Tomlinson defines the thermal efficiency η as the ratio of the measured instrument constant to the theoretical instrument constant where theoretical is defined to be the value obtained in the absence of any heat losses and diffusion effects. For the purposes of this report, η can be considered as $a_{1,\text{exptl.}}/a_{1,\text{theor.}}$. A further approximation was made in these calculations. The Tomlinson ΔS , the change in the shape factor caused by the proximity of the solvent and solution thermistors, was found to be very small for this system, that is, 0.015 cm, and was neglected. The agreement between the calculated and measured thermodynamic efficiencies is quite good as can be seen in Table 4. The apparatus constants used for these calculations are presented in Table 5. Attempts were made to preserve the notation of Tomlinson except where a conflict with other notations in this report arises. Table 6 presents the solvent constants. The general constants of Tomlinson are used as required. The agreement appears to be sufficiently good to state that the Tomlinson treatment of the thermal losses does account, quite well, for the observed thermodynamic efficiencies. In these calculations, the authors of this report have found little information concerning parameters such as thermal conductivity and diffusion coefficients for solvent vapors either pure or in the presence of air. The constants for ethyl acetate were substituted for those of 1,2-dimethoxyethane where needed (see Table 6). No transport information was found for 1,2-dichloroethane or for an analogous system.

The thermal conductivity of the solvent vapor-air mixture was calculated by the expression (Ref. 20)

$$k_{s-a} = \frac{X_s k_{s,s}^{1/3} + X_a k_{a,a}^{1/3}}{X_s M_s^{1/3} + X_a M_a^{1/3}}$$

In this expression, subscript s refers to solvent vapor at 37°C, subscript a refers to air at 37°C, and subscript s-a refers to the solvent vapor-air mixture at 37°C; and X is the mole fraction, k is the thermal conductivity, and M is the species molecular weight. For the purpose of these calculations, $k_a = 6.30 \times 10^{-5}$ cal/cm sec deg and the total pressure of the atmosphere was assumed to be 710 torr, the prevailing atmospheric pressure at the laboratory location.

TABLE 4. Calculated and Experimentally Determined Heat Losses

Solvent	Tomlinson (Ref. 12)			This work	
	Heat loss contributions			Efficiency, η calc.	a a_1 , theor., $\frac{\text{ohm-liter}}{\text{mole}}$
	Conduction through gas phase, c_v/ab	Radiation from drop, c_r/ab	Conduction through wire, c_w/ab		
Acetone.....	0.0506	0.0178	0.0196	0.919	485
1,2-Dichloroethane..	484
1,2-Dimethoxyethane.	0.222	0.063	0.069	0.738	601
Toluene.....	0.565	0.144	0.159	0.535	579

^a Calculated from equation in Ref. 4.^b $\eta_{\text{exptl.}} = 0.93$ has been reported for a Model 301 vapor pressure osmometer at 39°C (Ref. 1).

TABLE 5. Apparatus Constants Used in Calculating Thermodynamic Efficiencies According to Tomlinson (Ref. 12)

Constant	Value, cm
r_t (radius of thermistor bead).....	0.055
r_d (radius of drop).....	0.110
r_c (radius of cell).....	2.10
r_w (radius of stainless steel wire).....	0.005
l_c (length of cell).....	1.00
l_w (length of stainless steel wire).....	3.00
y (distance between thermistor axes)...	0.40
T_o (absolute temperature of cell).....	310.0 ^a
k_w (steel).....	0.111 ^b

^a In units of degrees Kelvin.

^b In units of cal/cm sec deg.

Of the factors used in the calculations, the least reliable were of the system geometry. Fortunately the computation can be carried out in such a manner that the results are not very sensitive to the errors in measurement of the cell dimensions. In the equation for the thermal loss the largest term is the loss caused by conduction through the vapor. This term contains the geometrical or shape factor. The relative contribution of this term can be obtained by dividing this term by a term also containing the shape factor, that is,

$$\eta = \frac{1}{1 + \frac{c_v + c_r + c_w}{ab}}$$

which is a rearranged form of Eq. 33 in Ref. 12. The consequence, therefore, is that the relative contribution of the largest contributor term is independent of the shape factor and dependent upon thermal constants. It is possible to vary the shape factor by 10% and not affect the thermodynamic efficiency by more than 0.4% when the thermodynamic efficiency is about 90%. The lower the thermodynamic efficiency, the smaller is the effect of shape-factor error. This latter fact is in accord with the nature of the experiment, since the radial distance to the solvent-saturated paper wall of the cell is different than the distance to the solvent-liquid cell surface. In addition, the distance to the liquid cell surface changes as successive readings are made. Further, the results of the calculations are rather insensitive with respect to the drop size, since only the smaller, radiant-heat-loss term is affected.

TABLE 6. Solvent Constants at 37°C

Solvent	Mol. wt., M, g/mole	Heat of vapor., ΔH_v , cal/mole	Density, d_{37}^0 , g/ml	Diff. coeff. into air D, cm ² /sec	Vapor pressure, p, torr	Thermal conductivity, $k_s \times 10^5$, cal/cm sec deg
Acetone.....	58.08	7,479 ^a	0.7706 ^b	0.150 ^c	377.7	2.91 ^d
1,2-Dichloro- ethane.....	98.97	8,014 ^e	1.2287 ^b
1,2-Dimethoxy- ethane.....	90.12	8,518 ^f	0.8480 ^g	0.0986 ^h	125.7	2.74 ⁱ
Toluene.....	92.13	9,004 ^j	0.8512 ^k	0.0974 ^c	51.5	3.79 ^l

^a Calculated from data in Ref. 21.^b Reference 22.^c Calculated from data in Ref. 23 using the equation $D = D_0 (T/T_0)^2 (p_0/p)$ where $T = 310^\circ\text{K}$, $p = 710$ torr, $T_0 = 273^\circ\text{K}$, $p_0 = 760$ torr, and $D_0 =$ diffusion coefficient at T_0 and p_0 .^d Reference 24.^e Reference 25.^f Calculated using the Antoine vapor pressure equation, $\log_{10} p$ (torr) = $7.2643 - 1379/(230 + t)$. The A and B constants were estimated using Cox chart intersection points and certain selected values of the boiling point.^g Reference 26.^h Calculated from data for ethyl acetate in Ref. 27 using the equation in footnote c above with $T_0 = 303^\circ\text{K}$.ⁱ Extrapolated value from data for ethyl acetate in Ref. 24.^j Calculated from data in Ref. 28.^k Reference 29.^l Reference 30.

In this term the effect should vary as the square of the drop radius but this dependence is somewhat lessened, since a function of the radius also exists in the shape factor.

DETERMINATION OF THE VAN LAAR HEAT OF MIXING β

Some significance can now be attached to the shape of the Δr vs. C plots. During the course of the measurements it became apparent that these curves were very reproducible and showed a degree of consistency. Plotting the data in the form of either Eq. 15a or 15b accounted for the data in a satisfactory manner. In calculating the heat-of-mixing term the form of the Van Laar equation was chosen for the sake of convenience and simplicity. It is realized that other more complex expressions may yield to better mechanistic interpretation of the heat of mixing particularly for systems that give negative values of β . In this report, however, this problem is not explored further. The value of the heat of vaporization used in the calculation of β is the quantity that the authors designated as the effective heat of vaporization ($\Delta H_{v,eff.} = \eta_{exptl.} \Delta H_v$) and is the value that is calculated from the experimental thermodynamic efficiency.

For the evaluation of the constant, β , the required solute densities were determined in wetting systems that had no effect upon the crystal. The data for fourteen solute-solvent systems are presented in Table 7. The negative value of β for bis(1,1,7-trihydroperfluoroheptyl) toluene-2,4-dicarbamate appears to be real and was obtained in two separate series of experiments. The reason for the unique behavior of this carbamate is not known although it may be related to a unique stiffness and consequent chain configuration.

OPERATION NOTES

In the course of the measurements made with the thermoelectric vapor pressure osmometer, some consideration should be made of the reading time that should be used. For most purposes, as long as solvent evaporation is prevented by proper syringe design and the instrument electronics are operating very well, the reading time is not critical for most solvents. The instrument as first received was sensitive to reading time. Reproducible results were only obtained when the reading time was within a few seconds of the elapsed time. In addition, long reading times (6-8 minutes) were required. The sensitivity was eliminated by replacing all of the electronic tubes even though all tubes were found to be within their design limits. Certain solvents such as the halogenated ones appeared to cause a drift. This drift is attributed to a time-dependent chemical change in the solvent. N,N-Dimethylformamide and 1,4-dioxane are two other solvents that show tendencies to drift.

TABLE 7. Van Laar Heats of Mixing Calculated from Second Virial Coefficients

Solute	Density d_{4}^{37} , g/ml	Heat of mixing β , kcal/mole			
		Acetone	1,2-Dichloro- ethane	1,2-Dimethoxy- ethane	Toluene
Acetanilide.....	1.208 ^a	2.67	4.66
1,3-Dinitrobenzene.....	1.54 ^b	2.84
Benzil.....	1.242 ^c	1.24	1.76	1.20	0.37
2,4,6-Tribromoaniline.....	2.590 ^c	2.41	0.80
Di-n-hexyl toluene-2,4-dicarbamate..	1.098 ^c	0.36
Bis(1,1-dihydroperfluorobutyl) toluene-2,4-dicarbamate.....	1.714 ^c	0.31
Bis(1,1,7-trihydroperfluoroheptyl) toluene-2,4-dicarbamate.....	1.820 ^c	-0.02	0.27
Bis(1,1,11-trihydroperfluoroundecyl) toluene-2,4-dicarbamate.....	1.955 ^a	0.11

^a Determined by displacement of Dow Corning 200 Fluid (d_{40}^{37} 0.9535).^b Estimated from literature and X-ray crystallographic data.^c Determined by displacement of water containing 0.1 wt. % 3M fluorochemical surfactant FX-176.

Some additional evidence as to the changes occurring in the solvent may be inferred from data obtained with a properly functioning instrument where the calibration constant a_1 is plotted as a function of time. Some solvents require short but others require long reading times. The data for the variation of a_1 with reading time are seen in Fig. 7. It can be seen that 6 minutes were required for 1,2-dimethoxyethane before the constant varied in a slow manner. Very short reading times could be used for toluene and acetone. The changes were sufficiently rapid for 1,2-dichloroethane to enable the use of a relatively short reading time. A number of factors not under control, such as oxygen, moisture, and gas solubility may be responsible for this effect. It should, however, be noted that the ordinate is drawn to an expanded scale and, within the accuracy of most calculations used in this report, the variations of the constant are not great. Such calibration curves may indeed be required for very precise work.

When the instrument was used intermittently a small but disturbing amount of experimental scatter was encountered. When measurements were made when the instrument was kept operating continuously, this scatter disappeared. A careful examination of the causes of this scatter led to a consideration of the characteristics of thermistors. Again, the observation of Müller and Stolten (Ref. 8) should be emphasized and provision for continuous excitation of the thermistors should be made in order to do very precise, quantitative work.

It is of interest to note the form of the pressure dependence of the coefficient of diffusion D (Table 6, footnote c). From this relationship, it can be anticipated that as the mean-free path of the vapor molecules is increased or, alternately, as the gas pressure is lowered, an increase in the thermodynamic efficiency can be obtained. This relationship is verified in the results of Higuchi et al. (Ref. 6). It can also be anticipated that since the solvent does have a finite vapor pressure and c_v , c_r , and c_w also have finite values, thermodynamic efficiencies of 1.00 will not be obtained. At the present time, as indicated previously, the vapor transport process and radiative and conductive heat losses appear to be adequate to account for the observed phenomenon. Additional corrections for solution mass and heat transport do not appear to be warranted. Furthermore, it can be anticipated that some of the observed scatter in much of the published data may be attributed to variations in atmospheric pressure. For example, a variation of 25 mm will cause a 1.7% change in the thermodynamic efficiency of toluene.

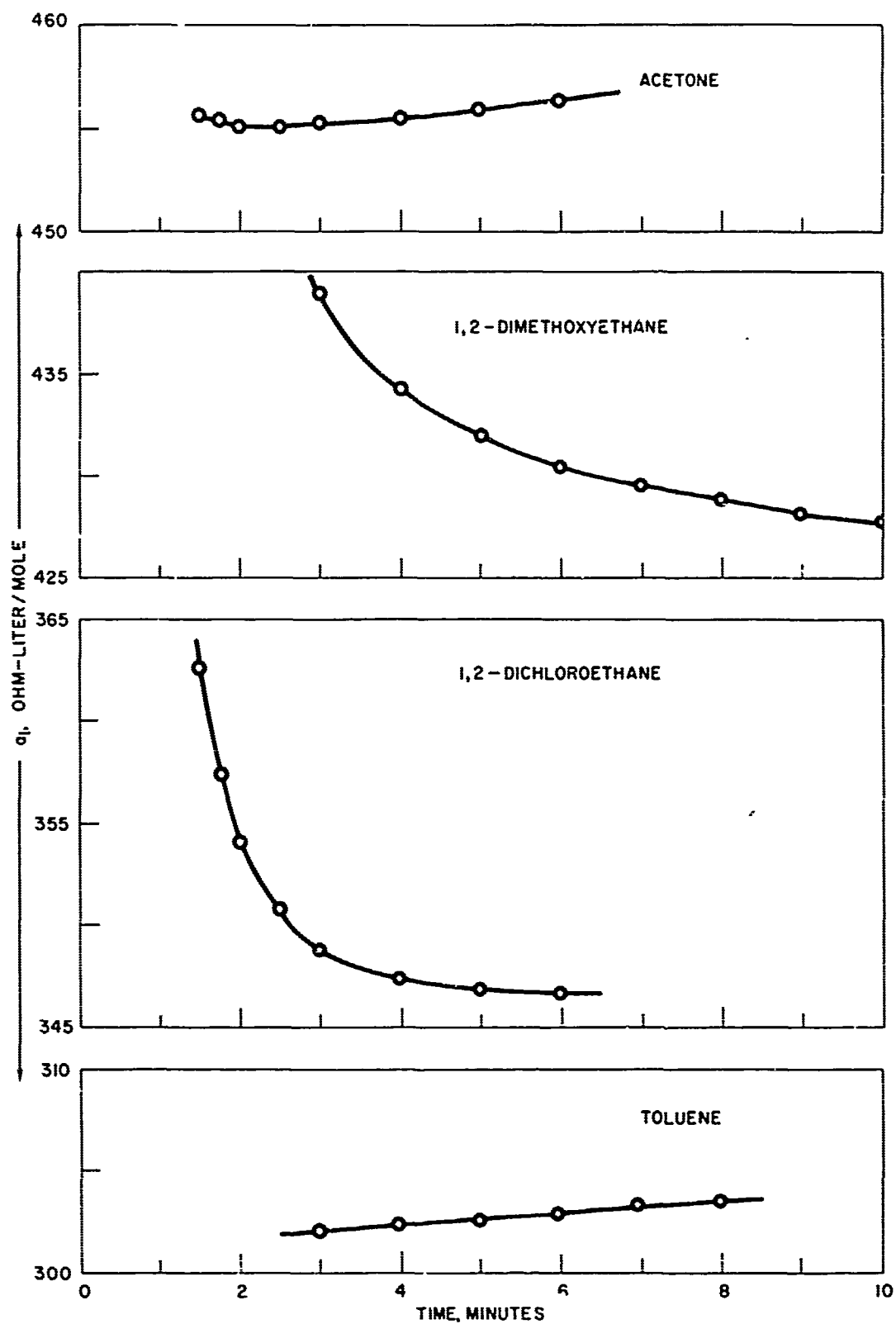


FIG. 7. Variation of the Calibration Constant, a_1 , With Time for Benzil in Various Solvents.

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ACKNOWLEDGMENT

The authors are indebted to C. Howard Shomate of this Station for writing the computer program and for many helpful discussions, and to the Hamilton Co. of Whittier, California, for generously providing the gas-tight syringes.

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3. REPORT TITLE		
THERMOELECTRIC VAPOR PRESSURE OSMOMETRY		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Research Report		
5. AUTHOR(S) (Last name, first name, initial)		
Adicoff, Arnold; Murbach, Warren J.		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1967	28	30
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)	
	NOTS TP 4247	
b. PROJECT NO.		
c. WEPTASK RMMP-22-066/216-1/R001-06-01 P.A. #2	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
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10. AVAILABILITY/LIMITATION NOTICES		
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<p>The thermoelectric vapor pressure osmometer is established as a satisfactory instrument for the determination of the vapor pressure lowering of solutes in solutions. The calibration constant, a_1, of the instrument is demonstrated to be independent of the nature of the solute and can be calculated from a knowledge of the system geometry and measurable thermodynamic and transport parameters.</p> <p>Experimental results are evaluated in terms of the change in resistance of the thermistor and the concentration of solution. It is necessary to use a second-degree equation in concentration plot to fit the data. Evaluation of the coefficient of the second-order term requires the incorporation of a heat-of-mixing term in the form of the Van Laar equation. The concentration-independent term B for the heat of mixing is obtained for fourteen solute-solvent pairs.</p>		

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